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(54) 【発明の名称】 インクジェット印刷用水系顔料インク組成物

(57) 【要約】

インクジェット印刷用水系顔料インク組成物に、特定の浸透剤と特定種のエマルジョンとを配合することによって、インクジェット印刷用インクの印刷特性を確保したまま、印刷対象物への顔料の浸透性と固着性を改善することが可能になった。

【発明の構成】 本発明は、顔料、水系分散媒体、分散剤の3成分を必須成分とするインクジェット印刷用水系顔料インク組成物に、さらに特定種の浸透剤すなわちアセチレングリコールかその誘導体と特定種のエマルジョン、すなわち、ポリウレタン系樹脂エマルジョンとを必須成分として配合したことを特徴とする顔料の浸透性と固着性に優れた新規インク組成物である。

【発明の効果】 特定種の浸透剤と特定種のエマルジョンを必須成分として選択配合したことにより、インクジェット印刷用水系顔料インクの印刷特性を確保したまま、印刷対象物への顔料の浸透性と固着性を改善することが可能になった。

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【特許請求の範囲】

【請求項 1】 (1) 顔料、(2) 水系分散媒体、(3) 顔料用分散剤、(4) ポリウレタン系樹脂を主体とする o/w 型エマルション粒子、および (5) アセチレングリコールかその誘導体の 5 種の必須成分からなることを特徴とするインクジェット印刷用水系顔料インク組成物。

【請求項 2】 アセチレングリコールが脂肪族炭化水素基を置換基として有するアセチレングリコールであり、誘導体が該アセチレングリコールのエチレンオキシドおよび/またはプロピレンオキシド付加物であることを特徴とする、請求項 1 に記載のインクジェット印刷用水系顔料インク組成物。

【請求項 3】 エマルション粒子の平均粒径が $0.3 \mu m$ 以下であることを特徴とする、請求項 1 または請求項 2 に記載のインクジェット印刷用水系顔料インク組成物。

【請求項 4】 エマルションが自己乳化型ポリウレタン系エマルションであることを特徴とする、請求項 1、2 または 3 に記載のインクジェット印刷用水系顔料インク組成物。

【請求項 5】 水系分散媒体が、エチレングリコール、ジエチレングリコール、トリエチレングリコール、プロピレングリコール、ジプロピレングリコール、グリセリンのいずれかである多価アルコールと水の混合液であることを特徴とする、請求項 1～4 のいずれかに記載のインクジェット印刷用水系顔料インク組成物。

【請求項 6】 インク組成物の pH が 6.5 以上 9.5 以下の範囲内にあることを特徴とする、請求項 1～5 のいずれかに記載のインクジェット印刷用水系顔料インク組成物。

【請求項 7】 インク組成物の必須成分の配合割合が、顔料はインク組成物全体に対して、有彩色有機顔料で 0.3 重量%以上 8.0 重量%以下、カーボンブラックで 1.0 重量%以上 12.0 重量%以下、分散剤は顔料に対して 20 重量%以上 80 重量%以下、エマルション樹脂は顔料の重量に対して 10 重量%以上 500 重量%以下、アセチレングリコールかその誘導体は顔料の重量に対して 2 重量%以上 500 重量%以下、媒体の一部である多価アルコールはインク組成物全体に対して 10 重量%以上 60 重量%以下の各範囲内にあつて、残余が水であり、インク組成物全体で 100 重量%となることを特徴とする、請求項 1～6 のいずれかに記載のインクジェット印刷用水系顔料インク組成物。

【請求項 8】 請求項 1～7 のいずれかに記載のインクジェット印刷用水系顔料インク組成物を用いてインクジェット印刷された記録物。

【発明の詳細な説明】

【0001】

【発明が属する技術分野】 本発明はインクジェット印刷

用水系顔料インク組成物に関するものであつて、より詳しくは良好な印刷特性、とくに透水性の印刷対象物に対して浸透性が優れていて鮮明で精細な高速印刷が可能であるという特性を有し、しかも印刷後にインクが印刷対象物上で乾燥すると、温水や界面活性剤入りの温水あるいは擦過に対して十分な耐久性を有して固着するように密着性の改善されたインクジェット印刷用水系顔料インク組成物に関するものである。

【0002】

【従来の技術】 インクジェット印刷用インク組成物として、水系で安全性が高く、顔料の耐水耐光性の良さが活用できるので望ましいとして、水系顔料インク組成物が種々提案されている。従来からの水系顔料インク組成物は、基本的には、顔料を水系媒体中に分散剤を用いて分散させた液組成物であり、インクジェット印刷に適するように、顔料粒径を小さく、かつ媒体中に安定に分散するよう適当な分散剤を選んで使用する等の工夫がなされている。しかし、布や紙に印刷した場合に、印刷物が水に濡れたり擦過されると、表面から顔料が移動・脱落して印刷物が汚染したり色落ちしたりする難点がある。とくに衣料用繊維品に印刷した場合、洗濯のたびにこの難点が深刻化してくるのである。鋭意検討の結果本発明者らは、インク組成物に o/w 型ポリウレタンエマルションを配合することでこの難点を解決することができるを見出し、特願 2001-285045 として特許出願した。しかし、さらに実用の場での検討を進めたところ、繊維製品へのインクジェット印刷において当該インクは繊維製品の単繊維間への浸透速度をより高めて鮮明精緻な印刷を、しかもより高速での印刷をも可能にすべきであることが判明した。

【0003】 一方、インクジェット印刷において、インクの印刷対象物内部への浸透速度を高めたり、その他のインク物性を適正化する手段として、種々の化合物の配合が古くから提案されてきている。その中で例えば、特公昭 58-6752 や特開昭 63-139964 ではアセチレングリコールやその誘導体をインクに配合することが提案されている。しかし、いずれの場合も o/w 型ポリウレタンエマルションとの併用の可否については何ら示唆していない。

【0004】

【発明が解決しようとする課題】 インクジェット印刷用インクとしての良好な印刷特性を有し、インクの印刷対象物内部への優れた浸透性と、印刷物において顔料が優れた耐久性・耐擦過性を有して密着している固着性とが両立するインクジェット印刷用水系顔料インク組成物の実現が本発明の課題である。

【0005】

【課題を解決するための手段】 インクジェット印刷用水系顔料インク組成物の組成、とりわけ、ポリウレタン樹脂エマルションを配合した水性顔料インクに配合する浸

透剤の選択で目的の達成を期する。

【0006】本発明のインク組成物は、顔料、水系媒体、顔料の分散剤、顔料固着用のエマルジョン樹脂、およびアセチレングリコールかその誘導体を必須成分とし、エマルジョン樹脂と浸透剤の組合せ選択により顔料粒子とエマルジョン粒子がともに安定に分散しているインクジェット印刷用水系顔料インク組成物であって、印刷時にインク液滴が長期に安定して吐出可能であり、紙や布である繊維製品の単繊維間への浸透速度が高く鮮明精緻な印刷を、しかもより高速で可能にし、印刷後に顔料が印刷対象物に高い耐水性と耐擦過性で密着する効果を発揮するものである。

【0007】従来からの本発明者らの経験に基づき、インク組成物中で顔料粒子とエマルジョン粒子がともに安定に分散するか否かは、(イ)調製したインク組成物を密栓ガラス容器内に入れて50℃の空気恒温槽内に7日間静置し、その前後で顔料やエマルジョン粒子の分散状態に変化がないことや、同じくインク組成物の粘度に変化がないことを判断基準とする加速分散安定性試験、

(ロ)同上試験を室温放置30日間で行う室温分散安定性試験で判断する。また、インク組成物の印刷特性に関しては、(ハ)調製したインク組成物をインクジェット印刷に供して、3時間連続印刷、その後1夜中断したのちにさらに1時間の連続印刷が、すべてのノズル孔でインクの吐出停止を伴わずに順調に行えたかをみる初期印刷試験、(ニ)同様に加速分散性試験後の印刷試験、

(ホ)同様に室温分散性試験後の印刷試験でインク組成物の印刷性を判断する。エマルジョン樹脂の顔料固着性に関しては、綿とエステル綿混の織物および編物を印刷対象品として行った、上記(ハ)(ニ)(ホ)の印刷試験片を、インク乾燥後に洗剤使用の温水洗濯試験機にて洗濯し、顔料の移行や脱落がないことを基準に(ヘ)温水洗濯試験で判断する。また、紙を印刷対象品とした場合には、インク乾燥後に印刷部分に水を滴下し、かつ指先で擦過して顔料の移行や脱落がないことを基準に

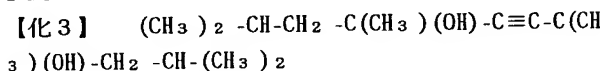
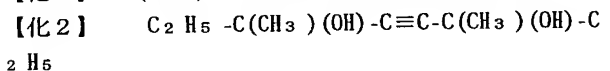
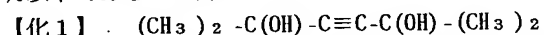
(ト)水濡れ擦過試験で判断する。(チ)上記印刷試験片を分解し顔料が繊維間や短繊維間に何処まで浸透したかを判定したり、(リ)インクジェット印刷試験でインクの吐出速度を、例えば、2000Hzから10000Hzまで変えて高速の印刷に対応可能か否かを判定した。以上のようにして目的達成の可否を判断した。

【0008】本発明で実施可能な顔料は、カーボンブラックおよび有機顔料である。金属化合物である無機顔料は比重が大きいことや表面活性のためか、本発明の技術範囲では無機顔料とエマルジョン粒子をともに安定に分散させることができず、目的とするインク組成物を実現することが不可能であった。本発明で好適に使用可能な顔料としては、各種製法によるカーボンブラック、アゾ系顔料、縮合アゾ系顔料、フタロシアニン系顔料、アントラキノン系顔料、ペリレン系顔料、ペリノン系顔料、

キナクリドン系顔料、ジオキサジン系、チオインジゴ系、イソインドリノン系顔料等である。これら顔料の具体例は、便覧等に収録されていて周知である。

【0009】本発明で使用される顔料は、最大粒子系0.8μm以下で平均粒径0.3μm以下の微細顔料が使用できる。とくに好適なのは最大粒子系0.5μm以下で平均粒径0.2μm以下の場合である。多くの市販顔料の中には、平均粒径が0.04μm以上0.15μm以下の範囲内であり、上記条件を満たすものがあるのが好都合である。顔料の配合割合は本発明のインク組成物中0.3重量%以上15.0重量%以下で配合する。通常目的の印刷では、有彩色有機顔料で2.0重量%以上8.0重量%以下が、カーボンブラックで6.0重量%以上12.0重量%以下が印刷物の着色濃度から好適である。しかし、淡色の場合は有彩色有機顔料で0.3重量%、カーボンブラックで1.0重量%以上が可能である。いずれの場合も顔料は単独または混合で使用する事が可能である。

【0010】本発明において、アセチレングリコールとは1,4-ビスアルキル-1,4-ビスヒドロキシ-2-ブチンであって、アルキルは直鎖または側鎖状の炭素数17以下の炭化水素基である。媒体組成によって異なるがインク組成物が均一であるためには、炭化水素基の炭素数は8以下が好ましい。これらアセチレングリコールの代表例としては、下記(化1)(化2)(化3)で表される化合物が挙げられる。本発明のインク組成物においてアセチレングリコールの配合割合は配合される顔料の重量に対して0.5重量%以上60.0重量%以下である。アセチレングリコール配合の効果をより有効にかつ無駄なく発揮させるためには2重量%以上50.0重量%以下であるのが好ましい。



【0011】本発明において、アセチレングリコール誘導体とは1,4-ビスアルキル-1,4-ビスヒドロキシ-2-ブチンのヒドロキシル基にエチレンオキシドおよび/またはプロピレンオキシドが付加物した化合物である。アルキルは直鎖または側鎖状の炭素数17以下の炭化水素基である。媒体組成によって異なるがインク組成物が均一であるためには、炭化水素基の炭素数は12以下が好ましい。エチレンオキシドおよび/またはプロピレンオキシドの付加モル数は総計で1以上30以下である。印刷物の耐水・耐擦過性から付加モル数は総計で2以上16以下であることが好ましい。本発明のインク組成物においてアセチレングリコール誘導体の配合割合は配合される顔料の重量に対して0.3重量%以上60.0重量%以下であるが、配合の効果をより有効にかつ無

駄なく発揮させるためには2重量%以上500重量%以下であるのが好ましい。

【0012】浸透剤として、例えば、ポリオキシエチレンラウリルエーテル系界面活性剤を用いる場合に比較すると、顔料の分散安定性は同等でありながら、本発明の場合の方が顔料インクが繊維間や短繊維間へ深く浸透しているし、印刷物表面の滲みが少なく、より鮮明で精細な印刷が可能である。また、より高速の印刷が可能である。インクの浸透性が向上した結果、印刷物の耐水・耐擦過性も向上していることが判明した。

【0013】本発明で実施可能なエマルション樹脂は、ポリウレタン系エマルション樹脂であって、インク調製原料として使用する際、または本発明のインク組成物調製後において、o/w型エマルションとして存在するものである。ポリウレタン系樹脂のエマルションには、比較的親水性の通常のポリウレタン系樹脂を、外部乳化剤を使用してエマルション化したものと、樹脂自体に乳化剤の働きをする官能基を共重合等の手段で導入した自己乳化型エマルションがある。いずれも実施可能であるが、インク組成物の成分の組み合わせによって、顔料およびエマルション粒子の分散安定性に若干の差
10 があるので注意を要する。顔料や分散剤との各種組み合わせにおいて、常に分散安定性に優れているのは自己乳化型エマルション樹脂、とりわけアミノカルボキシレート基等を有するアニオン型自己乳化型ポリウレタンのエマルション樹脂である。その際、ポリウレタンのソフトセグメントを問わず良好な分散安定性を示すが、印刷後の顔料の固着性ではソフトセグメントがポリカーボネート系である場合がとくに優れており、ソフトセグメントがポリエステル系の場合が前者について優れている。
20 ソフトセグメントがポリエーテル系の場合は、これらについて優れているが過激な使用分野においては懸念がある。ポリオキシエチレン鎖やシラノール基を側鎖に有する自己乳化型ポリウレタンエマルション樹脂や外部乳化型ポリウレタンエマルション樹脂も実施可能であるが、上記の場合に比較して分散安定性の劣る場合があるので注意を要する。エマルション樹脂の特性を表す指標として最低造膜温度や二次転移点がある。これらが、例えば、100℃を超えるような極端な場合を除き、零下から90℃の範囲内で実施可能である。最低造膜温度が0℃の場合でも順調に実施可能であった。40℃以下のより低温の場合ほどインクの固着速度が高い傾向があるが、インクの配合組成や配合比率の影響の方が大きいので、本発明では、エマルション樹脂の最低造膜温度や二次転移点には、必ずしもこだわらなくてよい。いずれにせよ、当該技術分野の技術者は、使用する顔料、分散剤、水系媒体、ポリウレタン系エマルション樹脂の組み合わせで、実験的に最適組成を選定することができるし、そのようにして本発明を実施するのが望ましい。後述の実施例で示すように、このような好適エマルション
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は市販品の中から選ぶことが可能である。

【0014】本発明におけるエマルション粒子は、平均粒径が0.01μm以上0.3μm以下の場合に好適に使用される。平均粒径が上記範囲を越えて大きい場合には、理由は定かではないが印刷を継続している途中で印刷機械は作動しているのにインクが吐出しなくなるトラブルが発生する場合がある。印刷機のノズル孔を含むインク流路を掃除して印刷再開可能となるが、これでは実用性を阻害することになる。また、平均粒径が上記範囲を越えて小さい場合には、前記のトラブルは発生しないが、エマルションが高コストで経済性に劣るので実施する意味がない。このような観点から、とくに好ましいエマルション粒子の平均粒径は0.03μm以上0.1μm以下の場合である。

【0015】エマルション樹脂の配合割合は、使用する顔料の重量に対して5重量%以上1000重量%以下で実施可能である。過剰の使用は顔料の被印刷体への固着性は申し分なく良好であるが、印刷性が劣るようになるので好ましくない。エマルション樹脂の使用量が過小の場合は印刷性は良好だが、固着性に劣るので好ましくない。このような次第で好適な範囲は、顔料の重量に対して10重量%以上500重量%以下、とくに好適なのは50重量%以上200重量%以下の範囲である。

【0016】本発明における水系媒体とは、エチレングリコール、ジエチレングリコール、トリエチレングリコール、プロピレングリコール、ジプロピレングリコール、グリセリンのいずれかである多価アルコールと水の混合物である。これら多価アルコールはエマルション粒子の安定性に有効であり、しかもインク組成物のインクジェット印刷機のノズル表面での乾燥固化を防止して、安定で順調なインクジェット印刷の実現に寄与するのである。例えば、類縁のグリコールエーテル、グリコールアセテート、グリコールエーテルアセテートでは、乾燥固化の防止作用は認められるものの、エマルション粒子が膨潤したり最終的に破壊してしまっ
て、しかもその間インク組成物の粘度が増大して本発明の目的を達成できない。その他の水溶性溶剤でも同様の現象が発生するので、多価アルコール以外の溶剤は不適当である。また、多価アルコールでも上記以外の多価アルコールではエマルション粒子の長期の安定性にやや劣るので好ましくない。本発明における水系媒体の多価アルコールは、インク組成物の分散安定性、インクジェット印刷機ごとの印刷特性、顔料の固着性等を勘案して、単独または混合で使用される。

【0017】本発明における水系媒体の一部である多価アルコールは、インク組成物中5.0重量%以上70.0重量%以下の割合で配合することが可能である。しかし、過小では前節の効果が少なく、過大では印刷物の顔料固着に悪影響を及ぼすので、10.0重量%以上50.0重量%以下の範囲で配合するのが好適である。水

の配合割合はインク組成中の水以外の必須成分を差し引いた残余である。水系媒体の配合割合や媒体中の水と多価アルコールの比率は、顔料、分散剤、エマルジョン粒子等の種類と配合割合に従って、実験的に最適化するの
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【0018】本発明における顔料の分散剤としては、従来から顔料を水媒体に分散させるのに有効な公知の分散剤の中から、エマルジョン粒子の分散に悪影響を及ぼさないもので、インクジェット印刷と印刷物の固着性に適したものを選んで配合する。この観点で本発明者らが実験的に選んだ好適な分散剤は、アニオン活性剤であるポリオキシエチレンアルキルエーテル硫酸エステル塩、同リン酸エステル塩、水溶性アクリル系樹脂、スチレン/マレイン酸系樹脂、スチレン/アクリル酸系樹脂、スチレン/ α -メチルスチレン/アクリル酸系樹脂等々である。ポリアクリル酸塩、ポリアクリルアミド、水溶性セルロース誘導体等は顔料の分散が不安定で不適当であつた。

【0019】本発明における顔料の分散剤のインク組成物中の配合割合は、使用する顔料に対して10重量%以上100重量%以下の範囲内である。過小では安定な分散効果を確保できないし、過大では飽和した分散効果に粘度増大による印刷機への不適合やコスト高など無用の悪影響を被るばかりである。このような観点から、好適な配合割合は顔料に対して20重量%以上80重量%以下の範囲内である。

【0020】以上に述べた本発明のインク組成物の必須成分の好適な配合割合を総括すると、顔料の配合割合はインク組成物全体に対して、有彩色有機顔料で0.3重量%以上8.0重量%以下、カーボンブラックで1.0重量%以上12.0重量%以下、分散剤は顔料に対して20重量%以上80重量%以下、エマルジョン樹脂は顔料の重量に対して10重量%以上500重量%以下、媒体の一部である多価アルコールはインク組成物全体に対して10重量%以上50重量%以下、アセチレングリコールかその誘導体は顔料の重量に対して2重量%以上500重量%以下、媒体の一部である多価アルコールはインク組成物全体に対して10重量%以上60重量%以下の各範囲内であって、残余が水であり、インク組成物全体で100重量%となる配合割合が好適である。

【0021】主にカーボンブラックを顔料として用いる場合であるが、調製したインク組成物のpHが低すぎたり、高すぎたりして顔料やエマルジョン粒子の長期の分散安定性が確保しがたい場合がある。このような場合にはインク組成物に微量の酸またはアルカリ性物質を添加してpHを6.5以上9.5以下の範囲内調節すると安定性が確保できる。このような例はカーボンブラック以外の有彩色有機顔料を用いる場合には稀あるが、顔料の合成方法によって遭遇することがある。この場合も前述と同様のpH調節を行って安定性を確保しておくのが好

ましい。

【0022】本発明のインク組成物は粘度5~20mPa・s、表面張力28~40mN/mであって、各種ピエゾ型インクジェット印刷機で好適に使用可能である。

【0023】本発明のインク組成物の製造方法を、その一例を挙げて説明する。顔料を水系媒体に分散させて顔料分散液を調製する。攪拌下のo/w型エマルジョンに顔料分散液を徐々に添加する。その際一度に急添するとエマルジョンが破壊されることがあるので注意を要する。ついで、水や多価アルコールを追加して全体の配合割合を所定値に調製する。本発明で用いるアセチレングリコールあるいはその誘導体は、顔料分散液の調製時に顔料分散液に添加して、またはエマルジョン液に添加して、あるいは多価アルコールに溶解してのいずれの段階において組成物中に配合することが可能である。アセチレングリコールあるいはその誘導体の溶解性挙動からすると、多価アルコールに溶解しての添加がもっとも無難である。組成物の配合完了後遠心分離や濾過によって粗大粒子や異物を除去する。この操作で配合割合が変動した場合には、所定値になるよう再調整する。またこの段階でインク組成物のpHを測定し、それが前項の範囲から逸脱していれば微量の酸性またはアルカリ性物質を添加してpHが好適な範囲内にあるよう調整する。得られたインク組成物は、先述の分散性試験、印刷試験、および固着性試験等で本発明の目的にかなうことを確認する。なお以上の別法として、濃厚なインク組成物を作っておき、使用に当たって水系触媒を添加して所定濃度に調整することも可能であるが、濃厚液では分散安定性に劣る場合があるので注意を要する。

【0024】以下に実施例を掲げて、本発明の詳細をより具体的に示す。インク組成物の評価は先述のように、調整したインク組成物の顔料およびエマルジョン粒子の分散安定性に関する(イ)加速分散安定性試験および(ロ)室温分散安定性試験を、印刷特性に関する(ハ)初期印刷試験、(ニ)加速分散性試験後の印刷試験、(ホ)室温分散性試験後の印刷試験を、エマルジョン樹脂の顔料固着性に関する、綿とエステル綿混の織物および編物を印刷対象品として行った、上記の印刷試験片を、インク乾燥後に洗剤使用の温水洗濯試験機にて洗濯し、顔料の移行や脱落の有無とその程度をみる(ヘ)温水洗濯試験、また、紙を印刷対象品とした場合の(ト)水漏れ擦過試験を実施した。また、(チ)上記印刷試験片を分解し顔料が繊維間や短繊維間に何処まで浸透したかを判定したり、(リ)インクジェット印刷試験でインクの吐出速度を、例えば、500Hzから5000Hzまで変えて高速の印刷に対応可能かを判定した。以上のようにして目的達成の可否を判断した。印刷試験はピエゾ素子を用いたインクジェット印刷機であるザール社製Xaarjet XJ128/360/55によって実施した。

【0025】（実施例1）黒色顔料であるカーボンブラック（C.I.ピグメントブラック7）60部、分散剤であるスチレン/ α -メチルスチレン/アクリル酸共重合体の30重量%溶液（ジョンソンポリマー製ジョンクリル70）70部、インクの保湿剤を兼ねる媒体であるエチレングリコール60部、防腐剤であるプロクセルLV2部、および水60部をボールミルに装填し、顔料の平均粒径が0.15 μ m以下になるよう100時間かけて顔料分散液を調製した。一方、ポリカーボネート型ポリウレタンエマルジョンの40重量%溶液（武田薬品工業製タケラックW-551/Tg35℃、平均エマルシ

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ン粒子径0.10 μ m）150部に、保湿剤を兼ねる媒体であるグリセリン100部、次いでジエチレングリコール300部を攪拌下に徐々に添加してエマルジョン液を調製した。エマルジョン液に顔料分散液を攪拌下に徐々に添加し、ついで、表面張力調整剤でもある浸透剤としてサーフィノール440（日信化学工業製、（化3）のエチレンオキシド3.5モル付加物）を純分で10部とpH調節剤のジエタノールアミン6部を、水82部とグリセリン100部の混合液に溶解した液を攪拌下に徐

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々に添加した（合計1000部）。遠心分離と濾過により粗大粒子を除去したが、インクの組成比率は実質的には変わらず、かくしてインク組成物の調製を完了した。えられたインク組成物は粘度が13.5mPa・s、表面張力が38.0mN/m、pHが9.0で、顔料およびエマルジョン粒子はともに微細に分散しており、加速分散性試験および室温分散性試験で、その安定性が確認できた。3種の印刷試験でも順調なジェット印刷が行えた。とくに吐出周波数を1000Hzから順次5000Hzにまで高めても順調なジェット印刷が行えた。印刷

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画像の境界は鮮明であり、顔料は繊維間とくに短繊維間にまでよく浸透していた。各種印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落はなかった。

【0026】（比較例1）実施例1における浸透剤をポリオキシエチレンラウリエテル系界面活性剤（第一工業製薬製ノイゲンET-143）に代え、組成比率は同じにして、実施例1の方法を繰り返した。えられたインク組成物で分散安定性や印刷特性も、印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落が起こらず満足すべきものであったが、顔料の短繊維間への浸透が実施例1の場合に比較して不十分であった。また、印刷画像の境界の鮮明さが実施例1の場合に比較して劣り、とくに吐出周波数が4000Hz以上ではその傾向が強くなった。

【0027】（比較例2）実施例1におけるエマルジョンを酢酸ビニル-アクリル共重合体樹脂エマルジョン（クラリアントポリマー製アプレタン2200/純分46重量%）に代え、組成比率は同じにして、実施例1の方法を繰り返した。えられたインク組成物で分散安定性

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や印刷特性は満たされ、顔料の短繊維間への浸透も良かったが、印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落が起こり不満足な結果に終わった。

【0028】（実施例2）黄色顔料であるジスアゾエロー（C.I.ピグメントイエロー17）30部、分散剤であるスチレン/ α -メチルスチレン/アクリル酸共重合体の34重量%溶液（ジョンソンポリマー製ジョンクリル62）35部、インクの保湿剤を兼ねる媒体であるグリセリン30部、防腐剤であるプロクセルLV2部、および水50部をビーズミルに装填し、5時間かけて顔料分散液を調製した。一方、ポリカーボネート型ポリウレタンエマルジョンの30重量%溶液（武田薬品工業製タケラックW-6010/Tg90℃、平均エマルシ

ン粒子径0.06 μ m）200部に、保湿剤を兼ねる媒体であるグリセリン170部、次いでジエチレングリコール300部、さらにpH調製剤のジエタノールアミン3部を攪拌下に徐々に添加してエマルジョン液を調製した。エマルジョン液に顔料分散液を攪拌下に徐々に添加し、ついで表面張力調整剤でもある浸透剤としてサーフィノール82（日信化学工業製、（化2）の化合物）を純分で15部とpH調節剤のジエタノールアミン5部を、水80部とグリセリン80部の混合液に溶解した液を攪拌下に徐々に添加した（合計1000部）。遠心分離と濾過により粗大粒子を除去したが、インクの組成比率は実質的には変わらず、かくしてインク組成物の調製を完了した。えられたインク組成物は粘度が10.3mPa・s、表面張力が35.7mN/m、pHが8.8

で、顔料およびエマルジョン粒子はともに微細に分散しており、加速分散安定性試験および室温分散安定性試験で、その安定性が確認できた。3種の印刷試験でも順調なジェット印刷が行えた。とくに吐出周波数を500Hzから順次5000Hzにまで高めても順調なジェット印刷が行えた。印刷画像の境界は鮮明であり、顔料は繊維間とくに短繊維間にまでよく浸透していた。各種印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落はなかった。

【0029】（比較例3）実施例2における浸透剤をポリオキシアルキレンイソデシルエーテル系界面活性剤（第一工業製薬製ノイゲンSDX-60）に代え、組成比率は同じにして、実施例2の方法を繰り返した。えられたインク組成物で分散安定性や印刷特性も、印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落が起こらず満足すべきものであったが、顔料の短繊維間への浸透が実施例2の場合に比較して不十分であった。また、印刷画像の境界の鮮明さが実施例2の場合に比較して劣り、とくに吐出周波数が4000Hz以上ではその傾向が強くなった。

【0030】（比較例4）実施例2におけるエマルジョンをアクリルシリコン樹脂エマルジョン（日本エヌエス

シー製カネビノールKD-3/純分26重量%、平均エマルジョン粒子径 $0.02\mu\text{m}$ に代え、組成比率は同じにして、実施例2の方法を繰り返した。調製当初のインク組成物で、顔料およびエマルジョンともに微細に分散をしていたが、加速分散安定性試験および室温分散安定性試験の途中で顔料の凝集や液の粘度の上昇が観察され、しかも初期印刷試験の途中でノズル孔の約20%でインクの吐出が停止した。

【0031】(実施例3) キナクリドン系赤色顔料であるC.I.ピグメントレッド122の40部、分散剤であるポリオキシエチレンアルキルエーテル硫酸エステルトリエタノールアミン塩(武田薬品製エマル20T)30部、インクの保湿剤を兼ねる媒体であるジエチレングリコール50部、防腐剤であるプロクセルLV2部、および水40部をボールミルに装填し、90時間かけて顔料分散液を調製した。一方、ポリエステル型ポリウレタンエマルジョンの35重量%溶液(武田薬品工業製タケラックW-7004/Tg 10°C 、平均エマルジョン粒子径 $0.08\mu\text{m}$)150部に、保湿剤を兼ねる媒体であるグリセリン100部、次いでジエチレングリコール250部を攪拌下に徐々に添加してエマルジョン液を調製した。この液にpH調製剤であるトリエタノールアミン4部とサーフィノール104(日信化学工業製、(化3)の化合物)の純分で10部を、水124部とグリセリン200部の混合液に溶解した液を攪拌下に徐々に添加し、ついで顔料分散液を添加した(合計1000部)。遠心分離と濾過により粗大粒子を除去したが、インクの組成比率は実質的には変わらず、かくしてインク組成物の調製を完了した。えられたインク組成物は粘度が $15.2\text{mPa}\cdot\text{s}$ 、表面張力が 31.0mN/m 、pHが8.7で、顔料およびエマルジョン粒子は共に微細に分散しており、加速分散安定性試験および室温分散安定性試験で、その安定性が確認できた。3種の印刷試験で、吐出周波数を500Hzから順次5000Hzにまで高めても順調なジェット印刷が行えた。印刷画像の境界は鮮明であり、顔料は繊維間とくに短繊維間にまでよく浸透していた。各種印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落はなかった。

【0032】(比較例5) 実施例3における浸透剤をポリオキシエチレンアルキルエーテル系界面活性剤(第一工業製薬製ノイゲンET-115)に代え、組成比率は同じにして、実施例3の方法を繰り返した。えられたインク組成物で分散安定性や印刷特性も、印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落が起こらず満足すべきものであったが、顔料の短繊維間への浸透が実施例3の場合に比較して不十分であった。また、印刷画像の境界の鮮明さが実施例3の場合に比較して劣り、とくに吐出周波数が4000Hz以上ではその傾向が強くなった。

【0033】(実施例4) 青色顔料であるフタロシアニンブルー(C.I.ピグメントブルー15:3)20部、分散剤であるポリオキシエチレンアルキルエーテルリン酸エステル(第一工業製薬製ブライサーF A215C/純分99重量%)6部、エチレングリコール25部、プロクセルLV2部、および水25部をビーズミルに装填し、6時間かけて顔料分散液を調製した。一方、ポリエステル型ポリウレタンエマルジョンの30重量%溶液(武田薬品工業製タケラックXW-75-C154/、平均エマルジョン粒子径 $0.075\mu\text{m}$)180部に、グリセリン100部、ジエチレングリコール300部、pH調製剤であるジエチルアミン2部とサーフィノール465(日信化学工業製、(化3)の化合物のエチレンオキシド10モル付加物)を純分で10部を水140部とグリセリン100部の混合液に溶解した液を順次攪拌下に徐々に添加し、エマルジョン液を調製した。このエマルジョン液に顔料分散液を攪拌下に徐々に添加した(合計1000部)。遠心分離と濾過により粗大粒子を除去したが、インクの組成比率は実質的には変わらず、かくしてインク組成物の調製を完了した。えられたインク組成物は粘度が $18.0\text{mPa}\cdot\text{s}$ 、表面張力が 32.9mN/m 、pHが9.0で、顔料およびエマルジョン粒子は共に微細に分散しており、加速分散安定性試験および室温分散安定性試験で、その安定性が確認できた。3種の印刷試験で吐出周波数を1000Hzから順次5000Hzにまで高めても順調なジェット印刷が行えた。印刷画像の境界は鮮明であり、顔料は繊維間とくに短繊維間にまでよく浸透していた。各種印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落はなかった。

【0034】(比較例6) 実施例4における浸透剤をポリオキシエチレンアルキルエーテル系界面活性剤(第一工業製薬製ノイゲンET-116C)に代え、組成比率は同じにして、実施例4の方法を繰り返した。えられたインク組成物で分散安定性や印刷特性も、印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落が起こらず満足すべきものであったが、顔料の短繊維間への浸透が実施例4の場合に比較して不十分であった。また、印刷画像の境界の鮮明さが実施例4の場合に比較して劣り、とくに吐出周波数が4000Hz以上ではその傾向が強くなった。

【0035】(比較例7) 実施例4における分散剤を水溶性セルロース誘導体であるヒドロキシプロピルセルロース(日本曹達製HPC-SL)に代えて、実施例4の方法を繰り返した。インク組成物は分散安定性が劣悪で、本発明が目的とするインク組成物としては失格であった。

【0036】(実施例5) 黒色顔料であるカーボンブラック(C.I.ピグメントブラック7)60部、分散剤であるスチレン/ α -メチルスチレン/アクリル酸共重合

体の30重量%溶液（ジョンソンポリマー製ジョンクリル70）70部、エチレングリコール60部、プロクセルLV2部、および水60部をボールミルに装填し、顔料の平均粒径が0.15 μ m以下になるよう100時間かけて顔料分散液を調製した。一方、ポリエステル型ポリウレタンエマルシヨンの35重量%溶液（日本エヌエスシー製RD20／最低造膜温度0℃、平均エマルシヨンの粒径0.08 μ m）150部に、グリセリン100部、次いでジエチレングリコール300部を攪拌下に徐々に添加してエマルシヨンを調製した。エマルシヨンの顔料分散液を攪拌下に徐々に添加し、ついでサーフイノール82（日信化学工業製、（化2）の化合物）を純分で10部とpH調節剤のジエタノールアミン4部を、水84部とグリセリン100部の混合液に溶解した液を攪拌下に徐々に添加した（合計1000部）。遠心分離と濾過により粗大粒子を除去したが、インクの組成比率は実質的には変わらず、かくしてインク組成物の調製を完了した。えられたインク組成物は粘度が16.5 mPa・s、表面張力が34.4 mN/m、pHが9.

1で、顔料およびエマルシヨンの粒子はともに微細に分散しており、加速分散安定性試験および室温分散安定性試験で、その安定性が確認できた。3種の印刷試験でも吐出周波数を500Hzから順次5000Hzにまで高めても順調なジェット印刷が行えた。印刷画像の境界は鮮明であり、顔料は繊維間とくに短繊維間にまでよく浸透していた。各種印刷試験片の温水洗濯試験および水漏れ擦過試験で、印刷物での顔料の移行や脱落はなかった。

【0037】（比較例8）実施例5の調製方法であるエマルシヨンの顔料分散液を添加するのを逆にして、顔料分散液にエマルシヨンを添加したところエマルシヨンの破壊が起こってしまい、目的とするインク組成物を調製することができなかった。

【発明の効果】特定種の浸透剤と特定種のエマルシヨンを必須成分として選択配合したことにより、インクジェット印刷用水系顔料インクの印刷特性を確保したまま、印刷対象物への顔料の浸透性と固着性を改善することが可能になった。

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CLAIMS

[Claim(s)]

[Claim 1] (1) The o/w mold emulsion particle which makes a subject a pigment, (2) drainage-system dispersion-medium object, the dispersant for (3) pigments, and (4) polyurethane system resin, and the ink jet printing water-system pigment ink constituent characterized by consisting of five sorts of indispensable components of (5) acetylene glycol or its derivative.

[Claim 2] The ink jet printing water-system pigment ink constituent according to claim 1 characterized by for an acetylene glycol being an acetylene glycol which has an aliphatic hydrocarbon radical as a substituent, and a derivative being the ethylene oxide and/or the propylene oxide addition product of this acetylene glycol.

[Claim 3] The ink jet printing water-system pigment ink constituent according to claim 1 or 2 characterized by the mean particle diameter of an emulsion particle being 0.3 micrometers or less.

[Claim 4] The ink jet printing water-system pigment ink constituent according to claim 1, 2, or 3 characterized by an emulsion being a self-emulsification mold polyurethane system emulsion.

[Claim 5] The ink jet printing water-system pigment ink constituent according to claim 1 to 4 characterized by a drainage system dispersion-medium object being the mixed liquor of ethylene glycol, a diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, the polyhydric alcohol that is either of the glycerols, and water.

[Claim 6] The ink jet printing water-system pigment ink constituent according to claim 1 to 5 characterized by pH of an ink constituent being within the limits of 9.5 or less [6.5 or more].

[Claim 7] As for a pigment, the blending ratio of coal of the indispensable component of an ink constituent receives the whole ink constituent: 12.0 or less % of the weight 1.0 % of the weight or more, by the chromatic color organic pigment, by carbon black 8.0 or less % of the weight 0.3% of the weight or more 500 or less % of the weight 10 % of the weight or more, in a dispersant, emulsion resin receives the weight of a pigment 80 or less % of the weight 20% of the weight or more to a pigment. 500 or less % of the weight 2 % of the weight or more, an acetylene glycol or its derivative receives the weight of a pigment. The polyhydric alcohol which is some media is in 60 or less % of the weight of each within the limits 10% of the weight or more to the whole ink constituent. The ink jet printing water-system pigment ink constituent according to claim 1 to 6 which the remainder is water and is characterized by becoming 100 % of the weight with the whole ink constituent.

[Claim 8] The record object by which ink jet printing was carried out using the ink jet printing water-system pigment ink constituent according to claim 1 to 7.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention should receive a more detailed good printing property, especially a permeable printing object about an ink jet printing water-system pigment ink constituent. When permeability is excellent, it has the property that clear and minute high-speed printing is possible and ink moreover dries on a printing object after printing, it is related with the ink jet printing water-system pigment ink constituent with which adhesion has been improved so that it may have sufficient endurance and may fix to warm water, the warm water containing a surfactant, or a scratch.

[0002]

[Description of the Prior Art] As an ink constituent for ink jet printing, safety is high at a drainage system, and the drainage system pigment ink constituent is variously proposed noting that it is desirable, since the goodness of the waterproof lightfastness of a pigment is utilizable. The device of a suitable dispersant being used for the drainage system pigment ink constituent from the former, choosing so that it may be the liquid constituent which the dispersant was used [constituent] and distributed the pigment in the drainage system medium fundamentally, and may be suitable for ink jet printing, and it may be small and pigment particle size may be distributed to stability in a medium is made. However, when it prints on cloth or paper, and printed matter is damp in water or it scrapes, there is a difficulty that a pigment moves and is omitted, and printed matter is polluted or decolored from a front face. When it prints in the fiber article for garments especially, this difficulty aggravates at every wash. this invention persons did patent application of this difficulty being solvable by blending an o/w mold polyurethane emulsion with an ink constituent as a header and an application for patent 2001-285045 wholeheartedly as a result of examination. However, when examination at the place of practical use was advanced further, in ink jet printing to textiles, the ink concerned raised the osmosis rate of a between [the single fibers of textiles] more, and it became clear clear minute printing that printing at a high speed should moreover also have been made possible more.

[0003] On the other hand, in ink jet printing, the osmosis rate inside [of ink] a printing object is raised, or combination of various compounds has been proposed as a means to rationalize other ink physical properties for many years. By JP,58-6752,B or JP,63-139964,A, blending an acetylene glycol and its derivative with ink is proposed in it. However, neither of the cases is suggested at all about the propriety of concomitant use with an o/w mold polyurethane emulsion.

[0004]

[Problem(s) to be Solved by the Invention] Implementation of the ink jet printing water-system pigment ink constituent with which it has a good printing property as ink for ink jet printing and with which the outstanding permeability inside [of ink] a printing object and the sticking tendency which had the endurance and scratch-proof nature in which the pigment was excellent in printed matter, and has been stuck are compatible is the technical problem of this invention.

[0005]

[Means for Solving the Problem] The target achievement is expected by selection of the penetrating agent blended with the watercolor pigment ink which blended the presentation of an ink jet printing water-system pigment ink constituent, division, and a polyurethane resin emulsion.

[0006] The ink constituent of this invention A pigment, a drainage system medium, the dispersant of a pigment, the emulsion resin for pigment fixing, And it is the ink jet printing water-system pigment ink constituent which uses an acetylene glycol or its derivative as an indispensable component, and both the pigment particle and the emulsion particle are distributing to stability by combination selection of emulsion resin and a penetrating agent. A liquid ink drop is stabilized at a long period of time at the time of printing, the regurgitation is possible, printing with the osmosis rate of a between [the single fibers of the textiles which are paper and cloth] minute vividly [it is high and] is enabled moreover more at high speed, and the effectiveness which a pigment sticks to a printing object by the high water resisting property and scratch-proof nature is demonstrated after printing.

[0007] Based on experience of this invention persons from the former, whether both a pigment particle and an emulsion particle distribute to stability in an ink constituent Put in the (b)-prepared ink constituent in sealing glassware, and it puts for seven days into a 50-degree C air thermostat. It judges by the acceleration distribution stability test which makes it a decision criterion that change will be in the distributed condition of a pigment or an emulsion particle before and behind that, or for there to be no change in the viscosity of an ink constituent similarly, and the room temperature distribution stability test which performs a (b) same-as-the-above trial between 30 days of room temperature neglect. Moreover, ink jet printing is presented with the ink constituent prepared (Ha) about the printing property of an ink constituent. After being interrupted continuation printing and after that 1 night for 3 hours, continuation printing of 1 more hour The printing nature of an ink constituent is judged by the printing trial after a room temperature dispersibility trial like the printing trial after an acceleration dispersibility trial, and (e) to the initial printing trial and this (2) appearance which find whether it was able to carry out favorably, without being accompanied by regurgitation halt of ink with no nozzle holes. About the pigment sticking tendency of emulsion resin, the printing test piece of the above-mentioned (Ha) (2) (**) which performed the textiles and knitting of cotton and ester cotton mix as elegance for printing is washed with the warm water laboratory washing machine of detergent use after ink desiccation, and is judged by warm water (passing) wash trial on the basis of there being no shift and omission of a pigment. Moreover, when paper is used as the elegance for printing, it judges by (g) ***** scratch trial on the basis of water being dropped at a printing part after ink desiccation, and scraping by the fingertip, and there being no shift and omission of a pigment. (h) It judged how far the above-mentioned printing test piece was disassembled and the pigment permeated between fiber and between staple fibers, and judged whether by ink jet (Li) printing trial, the regurgitation rate of ink could be changed from 2000Hz to 10000Hz, and it could respond to high-speed printing. The propriety of the purpose achievement was judged as mentioned above.

[0008] The pigments which can be carried out by this invention are carbon black and an organic pigment. The inorganic pigment which is metallic compounds cannot realize the ink constituent which stability cannot be made to distribute an inorganic pigment and an emulsion particle, but is made into the purpose in both the technical range of this invention for that specific gravity is large or surface activity. As an usable pigment, they are the carbon black by various processes, an azo system pigment, a condensation azo system pigment, a phthalocyanine system pigment, an anthraquinone system pigment, a perylene system pigment, a peri non system pigment, the Quinacridone system pigment, a dioxazine system, a thioindigo system, an isoindolinone system pigment, etc. suitably in this invention. The example of these pigments is recorded on the handbook etc. and is common knowledge.

[0009] A detailed pigment with a mean particle diameter of 0.3 micrometers or less can be used for the pigment used by this invention by 0.8 micrometers or less of grain-of-maximum-size systems. Especially a suitable thing is a case with a mean particle diameter of 0.2 micrometers or less in 0.5 micrometers or less of grain-of-maximum-size systems. In many commercial pigments, mean particle diameter is within the limits of 0.04 micrometers or more 0.15 micrometers or less, and since there are some which fulfill the above-mentioned conditions, it is convenient. The blending ratio of coal of a pigment is blended at 15.0 or less % of the weight 0.3% of the weight or more among the ink constituent of this invention. Usually, in printing of the purpose, 8.0 or less % of the weight 2.0 % of the weight or more is suitable for 12.0 or less % of the weight 6.0 % of the weight or more at carbon black from the coloring concentration of printed matter in a chromatic color organic pigment.

However, in the case of light color, 1.0 % of the weight or more is possible at carbon black 0.3% of the weight in a chromatic color organic pigment. In any case, it is possible that a pigment is independent or to use it by mixing.

[0010] In this invention, acetylene glycols are 1, the 4-bis-alkyl -1, and 4-bis-hydroxy-2-butene, and alkyl is a with a carbon number [of the shape of a straight chain or a side chain] of 17 or less hydrocarbon group. Although it changes with medium presentations, in order for the ink constituent to be uniform, as for the carbon number of a hydrocarbon group, eight or less are desirable. As an example of representation of these acetylene glycol, the compound expressed below (** 1) (** 2) (** 3) is mentioned. In the ink constituent of this invention, the blending ratio of coal of an acetylene glycol is 600 or less % of the weight 0.5 % of the weight or more to the weight of the pigment blended. In order to demonstrate the effectiveness of acetylene glycol combination that there is no futility more effectively, it is desirable that it is [2 % of the weight or more] 500 or less % of the weight.

[Formula 1] $(CH_3)_2-C(OH)-C^*C-C(OH)-(CH_3)_2$ [Formula 2] $C_2H_5-C(CH_3)(OH)-C^*C-C(CH_3)(OH)-C_2H_5$ [Formula 3] $(CH_3)_2-CH-CH_2-C(CH_3)(OH)-C^*C-C(CH_3)(OH)-CH_2-CH-(CH_3)_2$

[0011] In this invention, an acetylene glycol derivative is the compound in which ethylene oxide and/or propylene oxide carried out the addition product to the hydroxyl of 1, the 4-bis-alkyl -1, and 4-bis-hydroxy-2-butene. Alkyl is a with a carbon number [of the shape of a straight chain or a side chain] of 17 or less hydrocarbon group. Although it changes with medium presentations, in order for the ink constituent to be uniform, as for the carbon number of a hydrocarbon group, 12 or less are desirable. The number of addition mols of ethylene oxide and/or propylene oxide is 30 or less [1 or more] in the grand total. As for the deck watertight luminaire and the scratch-proof nature of printed matter to the number of addition mols, it is desirable that it is 16 or less [2 or more] in the grand total. Although it is 600 or less % of the weight 0.3 % of the weight or more to the weight of the pigment with which the blending ratio of coal of an acetylene glycol derivative is blended in the ink constituent of this invention, in order to demonstrate the effectiveness of combination that there is no futility more effectively, it is desirable that it is [2 % of the weight or more] 500 or less % of the weight.

[0012] As a penetrating agent, when using for example, a polyoxyethylene lauryl ether system surfactant, though the distributed stability of a pigment is equivalent, pigment ink has permeated [the direction in the case of this invention] between fiber and between staple fibers deeply, there are few blots of a printed matter front face, and clearer and minute printing is possible. Moreover, high-speed printing is more possible. It became clear that the deck watertight luminaire and the scratch-proof nature of printed matter were also improving as a result of the improvement of permeability of ink.

[0013] The emulsion resin which can be carried out by this invention is emulsion resin of a polyurethane system, and in case it is used as an ink preparation raw material, it exists as an emulsion of an o/w mold after ink constituent preparation of this invention. The emulsion of the self-emulsification mold which introduced the functional group which commits an emulsifier with means, such as copolymerization, is in resin itself at the emulsion of polyurethane system resin with some which emulsion-ized the usual polyurethane system resin of a hydrophilic property comparatively using the external emulsifier. Although all can be carried out, since some difference is in the distributed stability of a pigment and an emulsion particle, cautions are required with the combination of the component of an ink constituent. In various combination with a pigment or a dispersant, self-emulsification mold emulsion resin and the emulsion resin of the anion mold self-emulsification mold polyurethane which especially has an amino carboxylate radical etc. are always excellent in distributed stability. Although good distributed stability is shown regardless of the soft segment of polyurethane in that case, especially the case where a soft segment is a polycarbonate system is excellent in the sticking tendency of the pigment after printing, and, subsequently to the former, the case where a soft segment is a polyester system is excellent in it. When a soft segment is a polyether system, although subsequently to these excelled, there is concern in the excessive use field. Although self-emulsification mold polyurethane emulsion resin and external emulsification mold polyurethane emulsion resin which have a polyoxyethylene chain and a silanol group in a side chain can also be carried out, since distributed stability may be inferior as compared with the above-mentioned case, cautions are required. There are minimum film forming temperature and the second order transition point as an index showing the property of emulsion resin. These can carry out within

the limits of 90 degrees C from the freezing point except for an extreme case so that it may exceed 100 degrees C. Even when minimum film forming temperature was 0 degree C, it was able to carry out favorably. Although there is an inclination for the fixing rate of ink to be high, from that [40 degrees C or less] as the case of low temperature, since the effect of the combination presentation of ink or the rate of a compounding ratio is larger, it is not necessary to necessarily adhere to the minimum film forming temperature and the second order transition point of emulsion resin by this invention. Anyway, the engineer of the technical field concerned is the combination of the pigment to be used, a dispersant, a drainage system medium, and polyurethane system emulsion resin, and it is desirable to be able to select the optimal presentation experimentally, to make it such, and to carry out this invention. As the below-mentioned example shows, such a suitable emulsion can be chosen from commercial items.

[0014] The emulsion particle in this invention is suitably used, when mean particle diameter is 0.01 micrometers or more 0.3 micrometers or less. The trouble ink will not carry out [a trouble] the regurgitation to operating may generate a printing machine while continuing printing, although mean particle diameter of a reason is not certain across the above-mentioned range when large. Although the ink passage containing the nozzle hole of a printing machine is cleaned and resumption of printing is attained, practicality will be checked in this. Moreover, although a mean diameter does not generate the aforementioned trouble across the above-mentioned range in being small, there is no semantics carried out since an emulsion is inferior to economical efficiency at high cost. From such a viewpoint, especially the mean particle diameter of a desirable emulsion particle is the case of 0.03 micrometers or more 0.1 micrometers or less.

[0015] The blending ratio of coal of emulsion resin can be carried out at 1000 or less % of the weight 5% of the weight or more to the weight of the pigment to be used. Although it is good perfect, since superfluous use comes to be inferior in printing nature, it is not desirable. [of the sticking tendency to the printing hand-ed of a pigment] When too little [the amount of the emulsion resin used], although printing nature is good, since it is inferior to a sticking tendency, it is not desirable. 10-% of the weight or more 500 or less % of the weight and especially the suitable thing of the range suitable at such order are 50-% of the weight or more 200 or less % of the weight of the range to the weight of a pigment.

[0016] The drainage system medium in this invention is the mixture of ethylene glycol, a diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, the polyhydric alcohol that is either of the glycerols, and water. These polyhydric alcohol is effective in the stability of an emulsion particle, moreover prevents desiccation solidification in the nozzle front face of the ink jet printing machine of an ink constituent, and contributes it to implementation of stable and favorable ink jet printing. For example, of the glycol ether of a relative, glycol acetate, and glycol ether acetate, although a prevention operation of desiccation solidification is accepted, an emulsion particle swells, or finally it destroys, moreover the viscosity of an ink constituent increases in the meantime, and the purpose of this invention cannot be attained. Since a phenomenon with the same said of other water soluble solvents occurs, solvents other than polyhydric alcohol are unsuitable. Moreover, since polyhydric alcohol is also a little inferior to the long-term stability of an emulsion particle with polyhydric alcohol other than the above, it is not desirable. The polyhydric alcohol of the drainage system medium in this invention takes into consideration the distributed stability of an ink constituent, the printing property for every ink jet printing machine, the sticking tendency of a pigment, etc., and is used by independent or mixing.

[0017] The polyhydric alcohol which is some drainage system media in this invention can be blended at 70.0 or less % of the weight of a rate 5.0% of the weight or more among an ink constituent. However, if too little, there is little effectiveness of the foregoing paragraph, and since it has a bad influence on pigment fixing of printed matter if excessive, it is suitable to blend in 50.0 or less % of the weight of the range 10.0% of the weight or more. The blending ratio of coal of water is the remainder which deducted indispensable components other than the water under ink presentation. The blending ratio of coal of a drainage system medium, the water in a medium, and the ratio of polyhydric alcohol are good to optimize experimentally according to a class and the blending ratio of coal, such as a pigment, a dispersant, and an emulsion particle.

[0018] Out of a well-known dispersant effective in making a water medium distribute a pigment from

the former as a dispersant of the pigment in this invention, it does not have a bad influence on distribution of an emulsion particle, and the thing suitable for the sticking tendency of ink jet printing and printed matter is chosen and blended. The suitable dispersants which this invention persons chose experimentally in this viewpoint are **, such as the polyoxyethylene-alkyl-ether sulfate salt which is an anion activator, this phosphate, water-soluble acrylic resin, styrene / maleic-acid system resin, styrene / acrylic-acid system resin, and styrene / alpha methyl styrene / acrylic-acid system resin. Polyacrylate, polyacrylamide, a water-soluble cellulosic, etc. had unstable distribution of a pigment, and it was unsuitable.

[0019] The blending ratio of coal in the ink constituent of the dispersant of the pigment in this invention is 10 % of the weight or more of 100 or less % of the weight of within the limits to the pigment to be used. If too little, a stable dispersion effect cannot be secured, and unnecessary bad influences, such as nonconformance, cost quantity, etc. to a printing machine by viscosity increase, are just worn to the dispersion effect saturated if excessive. From such a viewpoint, the suitable blending ratio of coal is 20 % of the weight or more of 80 or less % of the weight of within the limits to a pigment.

[0020] If the blending ratio of coal with the suitable indispensable component of the ink constituent of this invention stated above is summarized 8.0 or less % of the weight 0.3 % of the weight or more, the blending ratio of coal of a pigment receives the whole ink constituent. By the chromatic color organic pigment 80 or less % of the weight 20 % of the weight or more, a dispersant receives a pigment 12.0 or less % of the weight 1.0% of the weight or more by carbon black. 500 or less % of the weight 10 % of the weight or more, emulsion resin receives the weight of a pigment. 50 or less % of the weight 10 % of the weight or more, the polyhydric alcohol which is some media receives the whole ink constituent. 500 or less % of the weight 2 % of the weight or more, an acetylene glycol or its derivative receives the weight of a pigment. The blending ratio of coal which it is 10 % of the weight or more of 60 or less % of the weight of each within the limits, and the remainder is water, and becomes 100 % of the weight with the whole ink constituent to the whole ink constituent is suitable for the polyhydric alcohol which is some media.

[0021] Although it is the case where carbon black is mainly used as a pigment, pH of the prepared ink constituent may be too low, or it is too high and may be hard to secure the long-term distributed stability of a pigment or an emulsion particle. In such a case, stability is securable, if the acid or alkaline substance of a minute amount is added to an ink constituent and pH is adjusted within the limits of 9.5 or less [6.5 or more]. When such an example uses chromatic color organic pigments other than carbon black, ***** may encounter by the synthetic approach of a pigment. It is desirable to perform the same pH accommodation as the above-mentioned also in this case, and to secure stability.

[0022] The ink constituents of this invention are viscosity 5 - 20 mPa-s, and surface tension 28 - 40 mN/m, and are suitably usable at various piezo mold ink jet printing machines.

[0023] The example is given and the manufacture approach of the ink constituent of this invention is explained. A drainage system medium is made to distribute a pigment and pigment dispersion liquid are prepared. Pigment dispersion liquid are gradually added to the o/w mold emulsion under stirring. Since an emulsion may be destroyed when it sudden-** at once in that case, cautions are required. Subsequently, water and polyhydric alcohol are added and the whole blending ratio of coal is prepared to a predetermined value. The acetylene glycol used by this invention or its derivative can be blended into a constituent in which phase which adds to pigment dispersion liquid at the time of preparation of pigment dispersion liquid, adds in emulsion liquid, or is dissolved in polyhydric alcohol. Considering an acetylene glycol or the soluble behavior of the derivative, the addition dissolved in polyhydric alcohol is the safest. The centrifugal separation after the completion of combination of a constituent and filtration remove a big and rough particle and a foreign matter. When the blending ratio of coal is changed by this actuation, it readjusts so that it may become a predetermined value. Moreover, pH of an ink constituent is measured in this phase, and if it has deviated from the range of the preceding clause, as the acidity of a minute amount or an alkaline substance is added and there is pH within suitable limits, it will adjust. It checks that the obtained ink constituent suits the purpose of this invention by the dispersibility trial of point **, a printing trial, sticking tendency trial, etc. In addition, although it is also possible to make the thick ink constituent as the above exception method, to add a

drainage system catalyst in use, and to adjust to predetermined concentration, since it may be inferior to distributed stability, a strong solution takes cautions.

[0024] An example is lifted to below and the detail of this invention is more concretely shown in it. Evaluation of an ink constituent the (b) acceleration distribution stability test and (b) room temperature distribution stability test about the pigment of the adjusted ink constituent, and the distributed stability of an emulsion particle like point **. The initial printing trial about a printing property (Ha), the printing trial after a (d) acceleration dispersibility trial, The printing trial after a (e) room temperature dispersibility trial is related with the pigment sticking tendency of emulsion resin. The above-mentioned printing test piece which performed the textiles and knitting of cotton and ester cotton mix as elegance for printing It washed with the warm water laboratory washing machine of detergent use after ink desiccation, and the (g) leak scratch trial at the time of using as the elegance for printing warm water wash trial which sees shift of a pigment, the existence, and extent of omission (passing), and paper was carried out. moreover, (**) — it judged how far the above-mentioned printing test piece was disassembled and the pigment permeated between fiber and between staple fibers, and judged whether by ink jet (Li) printing trial, the regurgitation rate of ink could be changed from 500Hz to 5000Hz, and it could respond to high-speed printing. The propriety of the purpose achievement was judged as mentioned above. A printing trial is Saar Xaarjet which used the piezo-electric element and which is an ink jet printing machine. It carried out by XJ128/360/55.

[0025] (Example 1) The ball mill was loaded with the carbon black (C. I. pigment black 7) 60 section which is a black pigment, the 30-% of the weight solution (JON krill 70 made from Johnson polymer) 70 section of the styrene / alpha methyl styrene / acrylic-acid copolymer which is a dispersant, the ethylene glycol 60 section which is the medium which serves as the moisturizer of ink, the pro KUSERU LV2 section which is antiseptics, and the water 60 section, and pigment dispersion liquid were prepared over 100 hours so that the mean particle diameter of a pigment might be set to 0.15 micrometers or less. the glycerol which is the medium which serves as a moisturizer in the 40-% of the weight solution (W-551/Tg35 degree-C [of the Takeda Chemical Industries bamboo racks], average emulsion particle diameter of 0.10 micrometers) 150 of a polycarbonate mold polyurethane emulsion section on the other hand — the 100 section, subsequently to the bottom of stirring of the diethylene-glycol 300 section it added gradually, and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in emulsion liquid, and the ten sections and the diethanolamine 6 section of a pH regulator were gradually added under stirring of the liquid which subsequently dissolved SAFI Norian 440 (the Nissin Chemical Industry make, 3.5 mol addition product of ethylene oxide of (**) 3)) by the pure part as a penetrating agent which is also a surface tension regulator at the mixed liquor of the water 82 section and the glycerol 100 section (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 13.5 mPa-s and surface tension are [38.0 mN/m and pH] 9.0, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration dispersibility trial and a room temperature dispersibility trial, and the obtained ink constituent has checked the stability. Jet printing also with three sorts of favorable printing trials was able to be performed. Even if it raised especially the regurgitation frequency even to 5000Hz one by one from 1000Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0026] (Example 1 of a comparison) Replacing the penetrating agent in an example 1 with the polyoxyethylene RAURI ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene ET- 143), the presentation ratio was made the same and repeated the approach of an example 1. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 1, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 1, it was inferior, and the

inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0027] (Example 2 of a comparison) Replacing the emulsion in an example 1 with the vinyl acetate-acrylic copolymer-resin emulsion (APURETAN 2200 made from the Clariant polymer/pure 46 % of the weight per part), the presentation ratio was made the same and repeated the approach of an example 1. Although distributed stability and a printing property were filled with the obtained ink constituent and osmosis of a between [the staple fibers of a pigment] was also good, it was the warm water wash trial of a printing test piece, and a leak scratch trial, and shift and omission of a pigment with printed matter took place, and it finished with the dissatisfied result.

[0028] (Example 2) The bead mill was loaded with the dysazo yellow (C. I. pigment yellow 17) 30 section which is a yellow pigment, the 34-% of the weight solution (JON krill 62 made from Johnson polymer) 35 section of the styrene / alpha methyl styrene / acrylic-acid copolymer which is a dispersant, the glycerol 30 section which is the medium which serves as the moisturizer of ink, the pro KUSERU LV2 section which is antiseptics, and the water 50 section, and pigment dispersion liquid were prepared over 5 hours. the glycerol 170 section which is the medium which serves as a moisturizer in the 30-% of the weight solution (W-6010/Tg90 degree-C [of the Takeda Chemical Industries bamboo racks], average emulsion particle diameter of 0.06 micrometers) 200 of a polycarbonate mold polyurethane emulsion section on the other hand — subsequently — a diethylene glycol — the 300 section, further, under stirring of the diethanolamine 3 section of pH modifier, it added gradually and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in emulsion liquid, and the 15 sections and the diethanolamine 5 section of a pH regulator were gradually added under stirring of the liquid which dissolved SAFI Norian 82 (the Nissin Chemical Industry make, compound of (** 2)) by the pure part as a penetrating agent which is subsequently also a surface tension regulator at the mixed liquor of the water 80 section and the glycerol 80 section (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 10.3 mPa-s and surface tension are [35.7 mN/m and pH] 8.8, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. Jet printing also with three sorts of favorable printing trials was able to be performed. Even if it raised especially the regurgitation frequency even to 5000Hz one by one from 500Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0029] (Example 3 of a comparison) Replacing the penetrating agent in an example 2 with the polyoxyalkylene isodecyl ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene SDX- 60), the presentation ratio was made the same and repeated the approach of an example 2. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 2, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 2, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0030] (Example 4 of a comparison) Replacing the emulsion in an example 2 with the acrylic silicon resin emulsion (Kane Vinol KDmade from Japanese ENUESUSHI- pure 3/26 % of the weight per part, average emulsion particle diameter of 0.02 micrometers), the presentation ratio was made the same and repeated the approach of an example 2. Although the pigment and the emulsion were distributing minutely with the ink constituent of the time of preparation, condensation of a pigment and the rise of the viscosity of liquid were observed in the middle of the acceleration distribution stability test and the room temperature distribution stability test, and, moreover, the regurgitation of ink stopped with about 20% of the nozzle hole in the middle of the initial printing trial.

[0031] (Example 3) The ball mill was loaded with the 40 sections of the C.I. pigment red 122 which is the Quinacridone system red pigments, the polyoxyethylene-alkyl-ether sulfate triethanolamine salt (Takeda Chemical EMARU 20 T) 30 section which is a dispersant, the diethylene-glycol 50 section

which is the medium which serves as the moisturizer of ink, the pro KUSERU LV2 section which is antiseptics, and the water 40 section, and pigment dispersion liquid were prepared over 90 hours. the glycerol which is the medium which serves as a moisturizer in the 35-% of the weight solution (W-7004/Tg10 degree-C [of the Takeda Chemical Industries bamboo racks], average emulsion particle diameter of 0.08 micrometers) 150 of a polyester mold polyurethane emulsion section on the other hand — the 100 section, subsequently to the bottom of stirring of the diethylene-glycol 250 section it added gradually, and emulsion liquid was prepared. ** which added gradually under stirring of the liquid which dissolved the ten sections in this liquid at the mixed liquor of the water 124 section and the glycerol 200 section by the pure part of the triethanolamine 4 section and SAFI Norian 104 (the Nissin Chemical Industry make, compound of (** 3)) which is pH modifier, and subsequently added pigment dispersion liquid (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 15.2 mPa-s and surface tension are [31.0 mN/m and pH] 8.7, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. By three sorts of printing trials, even if it raised the regurgitation frequency even to 5000Hz one by one from 500Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0032] (Example 5 of a comparison) Replacing the penetrating agent in an example 3 with the polyoxyethylene-alkyl-ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene ET- 115), the presentation ratio was made the same and repeated the approach of an example 3. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 3, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 3, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0033] (Example 4) The bead mill was loaded with the copper-phthalocyanine-blue (C. I. pigment blue 15:3) 20 section which is a blue pigment, the polyoxyethylene-alkyl-ether phosphoric ester (Dai-Ichi Kogyo Seiyaku ply surfboard A215C/pure 99 % of the weight per part) 6 section which is a dispersant, the ethylene glycol 25 section, the pro KUSERU LV2 section, and the water 25 section, and pigment dispersion liquid were prepared over 6 hours. on the other hand — the 30-% of the weight solution (Takeda Chemical Industries bamboo rack XW-75-C — 154/) of a polyester mold polyurethane emulsion In average emulsion particle diameter the 180 sections of 0.075 micrometers, the glycerol 100 section, the diethylene-glycol 300 section, the diethylamine 2 section which is pH modifier, and SAFI Norian 465 (the Nissin Chemical Industry make —) The liquid which dissolved the ten sections for the ten mol addition product of ethylene oxide of the compound of (** 3) in the mixed liquor of the water 140 section and the glycerol 100 section by the pure part was gradually added under sequential stirring, and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in this emulsion liquid (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 18.0 mPa-s and surface tension are [32.9 mN/m and pH] 9.0, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. Even if it raised the regurgitation frequency even to 5000Hz one by one from 1000Hz by three sorts of printing trials, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0034] (Example 6 of a comparison) Replacing the penetrating agent in an example 4 with the polyoxyethylene-alkyl-ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene ET-116C), the

presentation ratio was made the same and repeated the approach of an example 4. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 4, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 4, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0035] (Example 7 of a comparison) The dispersant in an example 4 was replaced with the hydroxypropylcellulose (Nippon Soda HPC-SL) which is a water-soluble cellulosic, and the approach of an example 4 was repeated. The ink constituent had inferior distributed stability and was disqualification as an ink constituent which this invention makes the purpose.

[0036] (Example 5) The ball mill was loaded with the carbon black (C. I. pigment black 7) 60 section which is a black pigment, the 30-% of the weight solution (JON krill 70 made from Johnson polymer) 70 section of the styrene / alpha methyl styrene / acrylic-acid copolymer which is a dispersant, the ethylene glycol 60 section, the pro KUSERU LV2 section, and the water 60 section, and pigment dispersion liquid were prepared over 100 hours so that the mean particle diameter of a pigment might be set to 0.15 micrometers or less. on the other hand — the 35-% of the weight solution (RD20/minimum-film-forming-temperature [of 0 degree C] made from Japanese ENUESUSHI, average emulsion particle size of 0.08 micrometers) 150 section of a polyester mold polyurethane emulsion — a glycerol — the 100 section, subsequently to the bottom of stirring of the diethylene-glycol 300 section it added gradually, and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in emulsion liquid, and, subsequently to the mixed liquor of the water 84 section and the glycerol 100 section, SAFI Norian 82 (the Nissin Chemical Industry make, compound of (** 2)) was gradually added by the pure part under stirring of the liquid which dissolved the ten sections and the diethanolamine 4 section of a pH regulator (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 16.5 mPa-s and surface tension are [34.4 mN/m and pH] 9.1, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. Even if three sorts of printing trials also raised the regurgitation frequency even to 5000Hz one by one from 500Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0037] (Example 8 of a comparison) It made it reverse to add pigment dispersion liquid in the emulsion liquid which is the preparation approach of an example 5, when emulsion liquid was added to pigment dispersion liquid, demulsification happened, and the ink constituent made into the purpose was not able to be prepared.

[Effect of the Invention] It became possible to improve the permeability and sticking tendency of a pigment to a printing object, securing the printing property of ink jet printing water-system pigment ink by having carried out selection combination by using the penetrating agent of a specific kind, and the emulsion of a specific kind as an indispensable component.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] This invention should receive a more detailed good printing property, especially a permeable printing object about an ink jet printing water-system pigment ink constituent. When permeability is excellent, it has the property that clear and minute high-speed printing is possible and ink moreover dries on a printing object after printing, it is related with the ink jet printing water-system pigment ink constituent with which adhesion has been improved so that it may have sufficient endurance and may fix to warm water, the warm water containing a surfactant, or a scratch.

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PRIOR ART

[Description of the Prior Art] As an ink constituent for ink jet printing, safety is high at a drainage system, and the drainage system pigment ink constituent is variously proposed noting that it is desirable, since the goodness of the waterproof lightfastness of a pigment is utilizable. The device of a suitable dispersant being used for the drainage system pigment ink constituent from the former, choosing so that it may be the liquid constituent which the dispersant was used [constituent] and distributed the pigment in the drainage system medium fundamentally, and may be suitable for ink jet printing, and it may be small and pigment particle size may be distributed to stability in a medium is made. However, when it prints on cloth or paper, and printed matter is damp in water or it scrapes, there is a difficulty that a pigment moves and is omitted, and printed matter is polluted or decolored from a front face. When it prints in the fiber article for garments especially, this difficulty aggravates at every wash. this invention persons did patent application of this difficulty being solvable by blending an o/w mold polyurethane emulsion with an ink constituent as a header and an application for patent 2001-285045 wholeheartedly as a result of examination. However, when examination at the place of practical use was advanced further, in ink jet printing to textiles, the ink concerned raised the osmosis rate of a between [the single fibers of textiles] more, and it became clear clear minute printing that printing at a high speed should moreover also have been made possible more.

[0003] On the other hand, in ink jet printing, the osmosis rate inside [of ink] a printing object is raised, or combination of various compounds has been proposed as a means to rationalize other ink physical properties for many years. By JP,58-6752,B or JP,63-139964,A, blending an acetylene glycol and its derivative with ink is proposed in it. However, neither of the cases is suggested at all about the propriety of concomitant use with an o/w mold polyurethane emulsion.

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EFFECT OF THE INVENTION

[Effect of the Invention] It became possible to improve the permeability and sticking tendency of a pigment to a printing object, securing the printing property of ink jet printing water-system pigment ink by having carried out selection combination by using the penetrating agent of a specific kind, and the emulsion of a specific kind as an indispensable component.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Implementation of the ink jet printing water-system pigment ink constituent with which it has a good printing property as ink for ink jet printing and with which the outstanding permeability inside [of ink] a printing object and the sticking tendency which had the endurance and scratch-proof nature in which the pigment was excellent in printed matter, and has been stuck are compatible is the technical problem of this invention.

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MEANS

[Means for Solving the Problem] The target achievement is expected by selection of the penetrating agent blended with the watercolor pigment ink which blended the presentation of an ink jet printing water-system pigment ink constituent, division, and a polyurethane resin emulsion.

[0006] The ink constituent of this invention A pigment, a drainage system medium, the dispersant of a pigment, the emulsion resin for pigment fixing, And it is the ink jet printing water-system pigment ink constituent which uses an acetylene glycol or its derivative as an indispensable component, and both the pigment particle and the emulsion particle are distributing to stability by combination selection of emulsion resin and a penetrating agent. A liquid ink drop is stabilized at a long period of time at the time of printing, the regurgitation is possible, printing with the osmosis rate of a between [the single fibers of the textiles which are paper and cloth] minute vividly [it is high and] is enabled moreover more at high speed, and the effectiveness which a pigment sticks to a printing object by the high water resisting property and scratch-proof nature is demonstrated after printing.

[0007] Based on experience of this invention persons from the former, whether both a pigment particle and an emulsion particle distribute to stability in an ink constituent Put in the (b)-prepared ink constituent in sealing glassware, and it puts for seven days into a 50-degree C air thermostat. It judges by the acceleration distribution stability test which makes it a decision criterion that change will be in the distributed condition of a pigment or an emulsion particle before and behind that, or for there to be no change in the viscosity of an ink constituent similarly, and the room temperature distribution stability test which performs a (b) same-as-the-above trial between 30 days of room temperature neglect. Moreover, ink jet printing is presented with the ink constituent prepared (Ha) about the printing property of an ink constituent. After being interrupted continuation printing and after that 1 night for 3 hours, continuation printing of 1 more hour The printing nature of an ink constituent is judged by the printing trial after a room temperature dispersibility trial like the printing trial after an acceleration dispersibility trial, and (e) to the initial printing trial and this (2) appearance which find whether it was able to carry out favorably, without being accompanied by regurgitation halt of ink with no nozzle holes. About the pigment sticking tendency of emulsion resin, the printing test piece of the above-mentioned (Ha) (2) (**) which performed the textiles and knitting of cotton and ester cotton mix as elegance for printing is washed with the warm water laboratory washing machine of detergent use after ink desiccation, and is judged by warm water (passing) wash trial on the basis of there being no shift and omission of a pigment. Moreover, when paper is used as the elegance for printing, it judges by (g) ***** scratch trial on the basis of water being dropped at a printing part after ink desiccation, and scraping by the fingertip, and there being no shift and omission of a pigment. (h) It judged how far the above-mentioned printing test piece was disassembled and the pigment permeated between fiber and between staple fibers, and judged whether by ink jet (Li) printing trial, the regurgitation rate of ink could be changed from 2000Hz to 10000Hz, and it could respond to high-speed printing. The propriety of the purpose achievement was judged as mentioned above.

[0008] The pigments which can be carried out by this invention are carbon black and an organic pigment. The inorganic pigment which is metallic compounds cannot realize the ink constituent which stability cannot be made to distribute an inorganic pigment and an emulsion particle, but is made into the purpose in both the technical range of this invention for that specific gravity is large or surface

activity. As an usable pigment, they are the carbon black by various processes, an azo system pigment, a condensation azo system pigment, a phthalocyanine system pigment, an anthraquinone system pigment, a perylene system pigment, a peri non system pigment, the Quinacridone system pigment, a dioxazine system, a thioindigo system, an isoindolinone system pigment, etc. suitably in this invention. The example of these pigments is recorded on the handbook etc. and is common knowledge.

[0009] A detailed pigment with a mean particle diameter of 0.3 micrometers or less can be used for the pigment used by this invention by 0.8 micrometers or less of grain-of-maximum-size systems. Especially a suitable thing is a case with a mean particle diameter of 0.2 micrometers or less in 0.5 micrometers or less of grain-of-maximum-size systems. In many commercial pigments, mean particle diameter is within the limits of 0.04 micrometers or more 0.15 micrometers or less, and since there are some which fulfill the above-mentioned conditions, it is convenient. The blending ratio of coal of a pigment is blended at 15.0 or less % of the weight 0.3% of the weight or more among the ink constituent of this invention. Usually, in printing of the purpose, 8.0 or less % of the weight 2.0 % of the weight or more is suitable for 12.0 or less % of the weight 6.0 % of the weight or more at carbon black from the coloring concentration of printed matter in a chromatic color organic pigment. However, in the case of light color, 1.0 % of the weight or more is possible at carbon black 0.3% of the weight in a chromatic color organic pigment. In any case, it is possible that a pigment is independent or to use it by mixing.

[0010] In this invention, acetylene glycols are 1, the 4-bis-alkyl -1, and 4-bis-hydroxy-2-butene, and alkyl is a with a carbon number [of the shape of a straight chain or a side chain] of 17 or less hydrocarbon group. Although it changes with medium presentations, in order for the ink constituent to be uniform, as for the carbon number of a hydrocarbon group, eight or less are desirable. As an example of representation of these acetylene glycol, the compound expressed below (** 1) (** 2) (** 3) is mentioned. In the ink constituent of this invention, the blending ratio of coal of an acetylene glycol is 600 or less % of the weight 0.5 % of the weight or more to the weight of the pigment blended. In order to demonstrate the effectiveness of acetylene glycol combination that there is no futility more effectively, it is desirable that it is [2 % of the weight or more] 500 or less % of the weight.

[Formula 1] $(CH_3)_2-C(OH)-C\equiv C-C(OH)-(CH_3)_2$ [Formula 2] $C_2H_5-C(CH_3)(OH)-C\equiv C-C(CH_3)(OH)-C_2H_5$ [Formula 3] $(CH_3)_2-CH-CH_2-C(CH_3)(OH)-C\equiv C-C(CH_3)(OH)-CH_2-CH-(CH_3)_2$

[0011] In this invention, an acetylene glycol derivative is the compound in which ethylene oxide and/or propylene oxide carried out the addition product to the hydroxyl of 1, the 4-bis-alkyl -1, and 4-bis-hydroxy-2-butene. Alkyl is a with a carbon number [of the shape of a straight chain or a side chain] of 17 or less hydrocarbon group. Although it changes with medium presentations, in order for the ink constituent to be uniform, as for the carbon number of a hydrocarbon group, 12 or less are desirable. The number of addition mols of ethylene oxide and/or propylene oxide is 30 or less [1 or more] in the grand total. As for the deck watertight luminaire and the scratch-proof nature of printed matter to the number of addition mols, it is desirable that it is 16 or less [2 or more] in the grand total. Although it is 600 or less % of the weight 0.3 % of the weight or more to the weight of the pigment with which the blending ratio of coal of an acetylene glycol derivative is blended in the ink constituent of this invention, in order to demonstrate the effectiveness of combination that there is no futility more effectively, it is desirable that it is [2 % of the weight or more] 500 or less % of the weight.

[0012] As a penetrating agent, when using for example, a polyoxyethylene lauryl ether system surfactant, though the distributed stability of a pigment is equivalent, pigment ink has permeated [the direction in the case of this invention] between fiber and between staple fibers deeply, there are few blots of a printed matter front face, and clearer and minute printing is possible. Moreover, high-speed printing is more possible. It became clear that the deck watertight luminaire and the scratch-proof nature of printed matter were also improving as a result of the improvement of permeability of ink.

[0013] The emulsion resin which can be carried out by this invention is emulsion resin of a polyurethane system, and in case it is used as an ink preparation raw material, it exists as an emulsion of an o/w mold after ink constituent preparation of this invention. The emulsion of the self-emulsification mold which introduced the functional group which commits an emulsifier with means, such as copolymerization, is in resin itself at the emulsion of polyurethane system resin with some

which emulsion-ized the usual polyurethane system resin of a hydrophilic property comparatively using the external emulsifier. Although all can be carried out, since some difference is in the distributed stability of a pigment and an emulsion particle, cautions are required with the combination of the component of an ink constituent. In various combination with a pigment or a dispersant, self-emulsification mold emulsion resin and the emulsion resin of the anion mold self-emulsification mold polyurethane which especially has an amino carboxylate radical etc. are always excellent in distributed stability. Although good distributed stability is shown regardless of the soft segment of polyurethane in that case, especially the case where a soft segment is a polycarbonate system is excellent in the sticking tendency of the pigment after printing, and, subsequently to the former, the case where a soft segment is a polyester system is excellent in it. When a soft segment is a polyether system, although subsequently to these excelled, there is concern in the excessive use field. Although self-emulsification mold polyurethane emulsion resin and external emulsification mold polyurethane emulsion resin which have a polyoxyethylene chain and a silanol group in a side chain can also be carried out, since distributed stability may be inferior as compared with the above-mentioned case, cautions are required. There are minimum film forming temperature and the second order transition point as an index showing the property of emulsion resin. These can carry out within the limits of 90 degrees C from the freezing point except for an extreme case so that it may exceed 100 degrees C. Even when minimum film forming temperature was 0 degree C, it was able to carry out favorably. Although there is an inclination for the fixing rate of ink to be high, from that [40 degrees C or less] as the case of low temperature, since the effect of the combination presentation of ink or the rate of a compounding ratio is larger, it is not necessary to necessarily adhere to the minimum film forming temperature and the second order transition point of emulsion resin by this invention. Anyway, the engineer of the technical field concerned is the combination of the pigment to be used, a dispersant, a drainage system medium, and polyurethane system emulsion resin, and it is desirable to be able to select the optimal presentation experimentally, to make it such, and to carry out this invention. As the below-mentioned example shows, such a suitable emulsion can be chosen from commercial items.

[0014] The emulsion particle in this invention is suitably used, when mean particle diameter is 0.01 micrometers or more 0.3 micrometers or less. The trouble ink will not carry out [a trouble] the regurgitation to operating may generate a printing machine while continuing printing, although mean particle diameter of a reason is not certain across the above-mentioned range when large. Although the ink passage containing the nozzle hole of a printing machine is cleaned and resumption of printing is attained, practicality will be checked in this. Moreover, although a mean diameter does not generate the aforementioned trouble across the above-mentioned range in being small, there is no semantics carried out since an emulsion is inferior to economical efficiency at high cost. From such a viewpoint, especially the mean particle diameter of a desirable emulsion particle is the case of 0.03 micrometers or more 0.1 micrometers or less.

[0015] The blending ratio of coal of emulsion resin can be carried out at 1000 or less % of the weight 5% of the weight or more to the weight of the pigment to be used. Although it is good perfect, since superfluous use comes to be inferior in printing nature, it is not desirable. [of the sticking tendency to the printing hand-ed of a pigment] When too little [the amount of the emulsion resin used], although printing nature is good, since it is inferior to a sticking tendency, it is not desirable. 10-% of the weight or more 500 or less % of the weight and especially the suitable thing of the range suitable at such order are 50-% of the weight or more 200 or less % of the weight of the range to the weight of a pigment.

[0016] The drainage system medium in this invention is the mixture of ethylene glycol, a diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, the polyhydric alcohol that is either of the glycerols, and water. These polyhydric alcohol is effective in the stability of an emulsion particle, moreover prevents desiccation solidification in the nozzle front face of the ink jet printing machine of an ink constituent, and contributes it to implementation of stable and favorable ink jet printing. For example, of the glycol ether of a relative, glycol acetate, and glycol ether acetate, although a prevention operation of desiccation solidification is accepted, an emulsion particle swells, or finally it destroys, moreover the viscosity of an ink constituent increases in the meantime, and the purpose of this invention cannot be attained. Since a phenomenon with the same said of other water soluble

solvents occurs, solvents other than polyhydric alcohol are unsuitable. Moreover, since polyhydric alcohol is also a little inferior to the long-term stability of an emulsion particle with polyhydric alcohol other than the above, it is not desirable. The polyhydric alcohol of the drainage system medium in this invention takes into consideration the distributed stability of an ink constituent, the printing property for every ink jet printing machine, the sticking tendency of a pigment, etc., and is used by independent or mixing.

[0017] The polyhydric alcohol which is some drainage system media in this invention can be blended at 70.0 or less % of the weight of a rate 5.0% of the weight or more among an ink constituent. However, if too little, there is little effectiveness of the foregoing paragraph, and since it has a bad influence on pigment fixing of printed matter if excessive, it is suitable to blend in 50.0 or less % of the weight of the range 10.0% of the weight or more. The blending ratio of coal of water is the remainder which deducted indispensable components other than the water under ink presentation. The blending ratio of coal of a drainage system medium, the water in a medium, and the ratio of polyhydric alcohol are good to optimize experimentally according to a class and the blending ratio of coal, such as a pigment, a dispersant, and an emulsion particle.

[0018] Out of a well-known dispersant effective in making a water medium distribute a pigment from the former as a dispersant of the pigment in this invention, it does not have a bad influence on distribution of an emulsion particle, and the thing suitable for the sticking tendency of ink jet printing and printed matter is chosen and blended. The suitable dispersants which this invention persons chose experimentally in this viewpoint are **, such as the polyoxyethylene-alkyl-ether sulfate salt which is an anion activator, this phosphate, water-soluble acrylic resin, styrene / maleic-acid system resin, styrene / acrylic-acid system resin, and styrene / alpha methyl styrene / acrylic-acid system resin. Polyacrylate, polyacrylamide, a water-soluble cellulosic, etc. had unstable distribution of a pigment, and it was unsuitable.

[0019] The blending ratio of coal in the ink constituent of the dispersant of the pigment in this invention is 10 % of the weight or more of 100 or less % of the weight of within the limits to the pigment to be used. If too little, a stable dispersion effect cannot be secured, and unnecessary bad influences, such as nonconformance, cost quantity, etc. to a printing machine by viscosity increase, are just worn to the dispersion effect saturated if excessive. From such a viewpoint, the suitable blending ratio of coal is 20 % of the weight or more of 80 or less % of the weight of within the limits to a pigment.

[0020] If the blending ratio of coal with the suitable indispensable component of the ink constituent of this invention stated above is summarized 8.0 or less % of the weight 0.3 % of the weight or more, the blending ratio of coal of a pigment receives the whole ink constituent. By the chromatic color organic pigment 80 or less % of the weight 20 % of the weight or more, a dispersant receives a pigment 12.0 or less % of the weight 1.0% of the weight or more by carbon black. 500 or less % of the weight 10 % of the weight or more, emulsion resin receives the weight of a pigment. 50 or less % of the weight 10 % of the weight or more, the polyhydric alcohol which is some media receives the whole ink constituent. 500 or less % of the weight 2 % of the weight or more, an acetylene glycol or its derivative receives the weight of a pigment. The blending ratio of coal which it is 10 % of the weight or more of 60 or less % of the weight of each within the limits, and the remainder is water, and becomes 100 % of the weight with the whole ink constituent to the whole ink constituent is suitable for the polyhydric alcohol which is some media.

[0021] Although it is the case where carbon black is mainly used as a pigment, pH of the prepared ink constituent may be too low, or it is too high and may be hard to secure the long-term distributed stability of a pigment or an emulsion particle. In such a case, stability is securable, if the acid or alkaline substance of a minute amount is added to an ink constituent and pH is adjusted within the limits of 9.5 or less [6.5 or more]. When such an example uses chromatic color organic pigments other than carbon black, ***** may encounter by the synthetic approach of a pigment. It is desirable to perform the same pH accommodation as the above-mentioned also in this case, and to secure stability.

[0022] The ink constituents of this invention are viscosity 5 - 20 mPa-s, and surface tension 28 - 40 mN/m, and are suitably usable at various piezo mold ink jet printing machines.

[0023] The example is given and the manufacture approach of the ink constituent of this invention is

explained. A drainage system medium is made to distribute a pigment and pigment dispersion liquid are prepared. Pigment dispersion liquid are gradually added to the o/w mold emulsion under stirring. Since an emulsion may be destroyed when it sudden-** at once in that case, cautions are required. Subsequently, water and polyhydric alcohol are added and the whole blending ratio of coal is prepared to a predetermined value. The acetylene glycol used by this invention or its derivative can be blended into a constituent in which phase which adds to pigment dispersion liquid at the time of preparation of pigment dispersion liquid, adds in emulsion liquid, or is dissolved in polyhydric alcohol. Considering an acetylene glycol or the soluble behavior of the derivative, the addition dissolved in polyhydric alcohol is the safest. The centrifugal separation after the completion of combination of a constituent and filtration remove a big and rough particle and a foreign matter. When the blending ratio of coal is changed by this actuation, it readjusts so that it may become a predetermined value. Moreover, pH of an ink constituent is measured in this phase, and if it has deviated from the range of the preceding clause, as the acidity of a minute amount or an alkaline substance is added and there is pH within suitable limits, it will adjust. It checks that the obtained ink constituent suits the purpose of this invention by the dispersibility trial of point **, a printing trial, sticking tendency trial, etc. In addition, although it is also possible to make the thick ink constituent as the above exception method, to add a drainage system catalyst in use, and to adjust to predetermined concentration, since it may be inferior to distributed stability, a strong solution takes cautions.

[0024] An example is lifted to below and the detail of this invention is more concretely shown in it. Evaluation of an ink constituent the (b) acceleration distribution stability test and (b) room temperature distribution stability test about the pigment of the adjusted ink constituent, and the distributed stability of an emulsion particle like point **. The initial printing trial about a printing property (Ha), the printing trial after a (d) acceleration dispersibility trial, The printing trial after a (e) room temperature dispersibility trial is related with the pigment sticking tendency of emulsion resin. The above-mentioned printing test piece which performed the textiles and knitting of cotton and ester cotton mix as elegance for printing It washed with the warm water laboratory washing machine of detergent use after ink desiccation, and the (g) leak scratch trial at the time of using as the elegance for printing warm water wash trial which sees shift of a pigment, the existence, and extent of omission (passing), and paper was carried out. moreover, (**) — it judged how far the above-mentioned printing test piece was disassembled and the pigment permeated between fiber and between staple fibers, and judged whether by ink jet (Li) printing trial, the regurgitation rate of ink could be changed from 500Hz to 5000Hz, and it could respond to high-speed printing. The propriety of the purpose achievement was judged as mentioned above. A printing trial is Saar Xaarjet which used the piezo-electric element and which is an ink jet printing machine. It carried out by XJ128/360/55.

[0025] (Example 1) The ball mill was loaded with the carbon black (C. I. pigment black 7) 60 section which is a black pigment, the 30-% of the weight solution (JON krill 70 made from Johnson polymer) 70 section of the styrene / alpha methyl styrene / acrylic-acid copolymer which is a dispersant, the ethylene glycol 60 section which is the medium which serves as the moisturizer of ink, the pro KUSERU LV2 section which is antiseptics, and the water 60 section, and pigment dispersion liquid were prepared over 100 hours so that the mean particle diameter of a pigment might be set to 0.15 micrometers or less. the glycerol which is the medium which serves as a moisturizer in the 40-% of the weight solution (W-551/Tg35 degree-C [of the Takeda Chemical Industries bamboo racks], average emulsion particle diameter of 0.10 micrometers) 150 of a polycarbonate mold polyurethane emulsion section on the other hand — the 100 section, subsequently to the bottom of stirring of the diethylene-glycol 300 section it added gradually, and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in emulsion liquid, and the ten sections and the diethanolamine 6 section of a pH regulator were gradually added under stirring of the liquid which subsequently dissolved SAFI Norian 440 (the Nissin Chemical Industry make, 3.5 mol addition product of ethylene oxide of (**) 3)) by the pure part as a penetrating agent which is also a surface tension regulator at the mixed liquor of the water 82 section and the glycerol 100 section (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 13.5 mPa-s and surface tension are [38.0 mN/m and pH] 9.0, viscosity is

distributing both the pigment and the emulsion particle minutely, and is an acceleration dispersibility trial and a room temperature dispersibility trial, and the obtained ink constituent has checked the stability. Jet printing also with three sorts of favorable printing trials was able to be performed. Even if it raised especially the regurgitation frequency even to 5000Hz one by one from 1000Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0026] (Example 1 of a comparison) Replacing the penetrating agent in an example 1 with the polyoxyethylene RAURI ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene ET- 143), the presentation ratio was made the same and repeated the approach of an example 1. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 1, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 1, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0027] (Example 2 of a comparison) Replacing the emulsion in an example 1 with the vinyl acetate-acrylic copolymer-resin emulsion (APURETAN 2200 made from the Clariant polymer/pure 46 % of the weight per part), the presentation ratio was made the same and repeated the approach of an example 1. Although distributed stability and a printing property were filled with the obtained ink constituent and osmosis of a between [the staple fibers of a pigment] was also good, it was the warm water wash trial of a printing test piece, and a leak scratch trial, and shift and omission of a pigment with printed matter took place, and it finished with the dissatisfied result.

[0028] (Example 2) The bead mill was loaded with the dysazo yellow (C. I. pigment yellow 17) 30 section which is a yellow pigment, the 34-% of the weight solution (JON krill 62 made from Johnson polymer) 35 section of the styrene / alpha methyl styrene / acrylic-acid copolymer which is a dispersant, the glycerol 30 section which is the medium which serves as the moisturizer of ink, the pro KUSERU LV2 section which is antiseptics, and the water 50 section, and pigment dispersion liquid were prepared over 5 hours. the glycerol 170 section which is the medium which serves as a moisturizer in the 30-% of the weight solution (W-6010/Tg90 degree-C [of the Takeda Chemical Industries bamboo racks], average emulsion particle diameter of 0.06 micrometers) 200 of a polycarbonate mold polyurethane emulsion section on the other hand — subsequently — a diethylene glycol — the 300 section, further, under stirring of the diethanolamine 3 section of pH modifier, it added gradually and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in emulsion liquid, and the 15 sections and the diethanolamine 5 section of a pH regulator were gradually added under stirring of the liquid which dissolved SAFI Norian 82 (the Nissin Chemical Industry make, compound of (** 2)) by the pure part as a penetrating agent which is subsequently also a surface tension regulator at the mixed liquor of the water 80 section and the glycerol 80 section (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 10.3 mPa-s and surface tension are [35.7 mN/m and pH] 8.8, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. Jet printing also with three sorts of favorable printing trials was able to be performed. Even if it raised especially the regurgitation frequency even to 5000Hz one by one from 500Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0029] (Example 3 of a comparison) Replacing the penetrating agent in an example 2 with the polyoxyalkylene isodecyl ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene SDX- 60), the presentation ratio was made the same and repeated the approach of an example 2. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared

with the case where it is an example 2, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 2, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0030] (Example 4 of a comparison) Replacing the emulsion in an example 2 with the acrylic silicon resin emulsion (Kane Vinol KD made from Japanese ENUESUSHI— pure 3/26 % of the weight per part, average emulsion particle diameter of 0.02 micrometers), the presentation ratio was made the same and repeated the approach of an example 2. Although the pigment and the emulsion were distributing minutely with the ink constituent of the time of preparation, condensation of a pigment and the rise of the viscosity of liquid were observed in the middle of the acceleration distribution stability test and the room temperature distribution stability test, and, moreover, the regurgitation of ink stopped with about 20% of the nozzle hole in the middle of the initial printing trial.

[0031] (Example 3) The ball mill was loaded with the 40 sections of the C.I. pigment red 122 which is the Quinacridone system red pigments, the polyoxyethylene-alkyl-ether sulfate triethanolamine salt (Takeda Chemical EMARU 20 T) 30 section which is a dispersant, the diethylene-glycol 50 section which is the medium which serves as the moisturizer of ink, the pro KUSERU LV2 section which is antiseptics, and the water 40 section, and pigment dispersion liquid were prepared over 90 hours. the glycerol which is the medium which serves as a moisturizer in the 35-% of the weight solution (W-7004/Tg10 degree-C [of the Takeda Chemical Industries bamboo racks], average emulsion particle diameter of 0.08 micrometers) 150 of a polyester mold polyurethane emulsion section on the other hand — the 100 section, subsequently to the bottom of stirring of the diethylene-glycol 250 section it added gradually, and emulsion liquid was prepared. ** which added gradually under stirring of the liquid which dissolved the ten sections in this liquid at the mixed liquor of the water 124 section and the glycerol 200 section by the pure part of the triethanolamine 4 section and SAFI Norian 104 (the Nissin Chemical Industry make, compound of (** 3)) which is pH modifier, and subsequently added pigment dispersion liquid (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 15.2 mPa-s and surface tension are [31.0 mN/m and pH] 8.7, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. By three sorts of printing trials, even if it raised the regurgitation frequency even to 5000Hz one by one from 500Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0032] (Example 5 of a comparison) Replacing the penetrating agent in an example 3 with the polyoxyethylene-alkyl-ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene ET- 115), the presentation ratio was made the same and repeated the approach of an example 3. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 3, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 3, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0033] (Example 4) The bead mill was loaded with the copper-phthalocyanine-blue (C. I. pigment blue 15:3) 20 section which is a blue pigment, the polyoxyethylene-alkyl-ether phosphoric ester (Dai-Ichi Kogyo Seiyaku ply surfboard A215C/pure 99 % of the weight per part) 6 section which is a dispersant, the ethylene glycol 25 section, the pro KUSERU LV2 section, and the water 25 section, and pigment dispersion liquid were prepared over 6 hours. on the other hand — the 30-% of the weight solution (Takeda Chemical Industries bamboo rack XW-75-C — 154/) of a polyester mold polyurethane emulsion In average emulsion particle diameter the 180 sections of 0.075 micrometers, the glycerol 100 section, the diethylene-glycol 300 section, the diethylamine 2 section which is pH modifier, and SAFI Norian 465 (the Nissin Chemical Industry make —) The liquid which dissolved the ten sections

for the ten mol addition product of ethylene oxide of the compound of (** 3) in the mixed liquor of the water 140 section and the glycerol 100 section by the pure part was gradually added under sequential stirring, and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in this emulsion liquid (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 18.0 mPa-s and surface tension are [32.9 mN/m and pH] 9.0, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. Even if it raised the regurgitation frequency even to 5000Hz one by one from 1000Hz by three sorts of printing trials, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0034] (Example 6 of a comparison) Replacing the penetrating agent in an example 4 with the polyoxyethylene-alkyl-ether system surfactant (Dai-Ichi Kogyo Seiyaku noy gene ET-116C), the presentation ratio was made the same and repeated the approach of an example 4. The obtained ink constituent of osmosis of a between [the staple fibers of a pigment] was inadequate as compared with the case where it is an example 4, although shift or omission of a pigment with printed matter did not take place but it should be satisfied with the warm water wash trial of a printing test piece, and the leak scratch trial of distributed stability and a printing property. Moreover, as compared with the case where the clearness of the boundary of a printing image is an example 4, it was inferior, and the inclination became [especially the regurgitation frequency] strong above 4000Hz.

[0035] (Example 7 of a comparison) The dispersant in an example 4 was replaced with the hydroxypropylcellulose (Nippon Soda HPC-SL) which is a water-soluble cellulosic, and the approach of an example 4 was repeated. The ink constituent had inferior distributed stability and was disqualification as an ink constituent which this invention makes the purpose.

[0036] (Example 5) The ball mill was loaded with the carbon black (C. I. pigment black 7) 60 section which is a black pigment, the 30-% of the weight solution (JON krill 70 made from Johnson polymer) 70 section of the styrene / alpha methyl styrene / acrylic-acid copolymer which is a dispersant, the ethylene glycol 60 section, the pro KUSERU LV2 section, and the water 60 section, and pigment dispersion liquid were prepared over 100 hours so that the mean particle diameter of a pigment might be set to 0.15 micrometers or less. on the other hand — the 35-% of the weight solution (RD20/minimum-film-forming-temperature [of 0 degree C] made from Japanese ENUESUSHI, average emulsion particle size of 0.08 micrometers) 150 section of a polyester mold polyurethane emulsion — a glycerol — the 100 section, subsequently to the bottom of stirring of the diethylene-glycol 300 section it added gradually, and emulsion liquid was prepared. It added gradually under stirring of pigment dispersion liquid in emulsion liquid, and, subsequently to the mixed liquor of the water 84 section and the glycerol 100 section, SAFI Norian 82 (the Nissin Chemical Industry make, compound of (** 2)) was gradually added by the pure part under stirring of the liquid which dissolved the ten sections and the diethanolamine 4 section of a pH regulator (a total of 1000 sections). Although centrifugal separation and filtration removed the big and rough particle, substantially, the presentation ratio of ink did not change but completed preparation of an ink constituent in this way. 16.5 mPa-s and surface tension are [34.4 mN/m and pH] 9.1, viscosity is distributing both the pigment and the emulsion particle minutely, and is an acceleration distribution stability test and a room temperature distribution stability test, and the obtained ink constituent has checked the stability. Even if three sorts of printing trials also raised the regurgitation frequency even to 5000Hz one by one from 500Hz, favorable jet printing was able to be performed. The boundary of a printing image is clear and the pigment had permeated well even especially between staple fibers between fiber. At the warm water wash trial of various printing test pieces, and a leak scratch trial, there were no shift and omission of a pigment with printed matter.

[0037] (Example 8 of a comparison) It made it reverse to add pigment dispersion liquid in the emulsion liquid which is the preparation approach of an example 5, when emulsion liquid was added to pigment dispersion liquid, demulsification happened, and the ink constituent made into the purpose

was not able to be prepared.

[Translation done.]

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